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THE CHEMISTRY AND APPLICATIONS FOR THE SOLUBILIZATION OF CHROMA--ETC(U)

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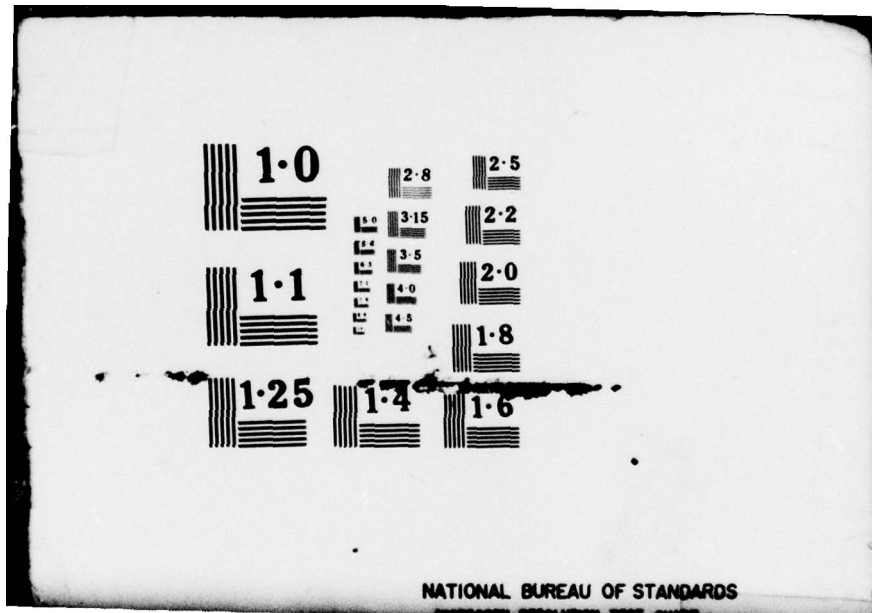
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THE CHEMISTRY AND APPLICATIONS FOR THE SOLUBILIZATION  
OF CHROMATE SALTS IN NONPOLAR ORGANIC MEDIA - PART III

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23 MARCH 1979

PHASE REPORT  
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## I N T R O D U C T I O N

This report discusses the application of the concept of phase transfer catalysis to the development of an organo-soluble corrosion inhibitor containing chromium VI. For the first time, transparent organic protective coatings containing dissolved chromium VI have been formulated; prior use of chromium VI required dispersions of large amounts of chromates which rendered the film opaque. In addition, the new inhibitor has proven to be an excellent oxidizing agent in organic media. The work reported herein was conducted under AIRTASK NO. R01309, IR Work Unit GC 171.

## S U M M A R Y   O F   R E S U L T S

1. A novel corrosion inhibitor (herein called soluble dichromate or SDC) has been prepared with the following characteristics:
  - a. Contains 11% chromium VI - one of the most effective corrosion inhibitors for steel and aluminum.
  - b. Excellent storage stability at room temperature - previous attempts at preparing soluble dichromate were unsuccessful due to autooxidation.
  - c. Soluble in aromatic and chlorinated hydrocarbons, alcohols, ketones, and acetates; however, solution stability is limited in certain solvents.
2. The following materials, modified with SDC just prior to use, exhibit marked improvement in their ability to protect aircraft metals in short term salt spray tests: MIL-C-85054 (Amlguard) corrosion preventive compound, an epoxy/polyamide coating, MIL-E-5557 alkyd enamel, and MIL-C-81309 ultra thin film corrosion preventive compound.
3. Because chromium VI is an oxidizing agent, SDC was used successfully to accelerate the cure of a polysulfide sealant base.

## C O N C L U S I O N S

1. The addition of SDC to protective coatings just prior to application is an inexpensive, facile, effective technique for upgrading corrosion inhibitive performance of coatings and corrosion preventive compounds without seriously affecting the appearance of the dried film.
2. In addition, SDC may find further application as an accelerator for sealant formulations.

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R E C O M M E N D A T I O N S

The scope of this investigation was limited to chromate and dichromate anions. Other inhibitive anions (molybdates, borates, silicates, etc.) as well as oxidative anions (nitrates, permanganates, etc.) can and should be investigated for potential application to Naval materials problems.

## T A B L E O F C O N T E N T S

	<u>Page No.</u>
SUMMARY	
Introduction . . . . .	1
Summary of Results . . . . .	1
Conclusions . . . . .	1
Recommendations . . . . .	2
 LIST OF TABLES . . . . .	 4
LIST OF FIGURES . . . . .	4
BACKGROUND . . . . .	5
CHEMISTRY OF PHASE TRANSFER CATALYSTS . . . . .	6
RESULTS . . . . .	7
DISCUSSION OF RESULTS . . . . .	15
EXPERIMENTAL . . . . .	17
CONCLUSIONS . . . . .	19
RECOMMENDATIONS . . . . .	19
REFERENCES . . . . .	20
ACKNOWLEDGEMENT . . . . .	21



L I S T O F T A B L E S

<u>Table No.</u>		<u>Page No.</u>
I	Phase Transfer Catalysts . . . . .	7
II	Chromate Transfer . . . . .	8
III	Dichromate Transfer . . . . .	9
IV	Experimental Coatings. . . . .	18

L I S T O F F I G U R E S

<u>Figure No.</u>		
1.	Soluble Dichromate Modified MIL-C-85054 . . .	11
2.	Soluble Dichromate Modified Epoxy/Polyamide Coating	12
3.	Soluble Dichromate Modified MIL-E-5557 . . .	13
4.	Soluble Dichromate Modified MIL-C-81309 . . .	14

## B A C K G R O U N D

A previous in-house independent research project, Work Unit GC312, dealt with the chemical modification of corrosion inhibiting chromate salts for addition to liquid organic materials such as paint formulations. Its objective was to utilize new concepts in organic chemistry (references (a)-(f)) towards improving the corrosion protection afforded by these coatings. Inorganic salts were to be complexed with macrocyclic polyethers in order to render them soluble in the organic media. Dissolved chromium VI should not be confused with dispersed chromate pigments used in metal primer coatings. While the latter consists of discrete particles within the paint film awaiting release by leaching or physical disruption of the film, the former is uniformly distributed throughout the film, possibly chemisorbed by the substrate. Although not considered to be useful for primer coatings, it was thought that dissolved chromium VI would enhance the salt spray characteristics of uninhibited or transparent specialty coatings.

The initial research was promising, as reported in reference (g). Aircraft enamels containing small amounts of dissolved chromate provided definite protection to aluminum, steel, and magnesium test panels in long term salt spray tests. On the negative side, two serious problems prevented successful fleet use of the idea: the complexed chromate salt had too short a shelf life to be compatible with field use and the complexed salt was not sufficiently soluble in organic media less polar than paint vehicles - i.e., fuels, lubricants, etc. In addition, the macrocyclic reagents were expensive. Therefore, it was recommended in reference (h) that the project be terminated but reactivated at such time that it appeared both feasible and practicable to solubilize inorganic inhibitors using new techniques.

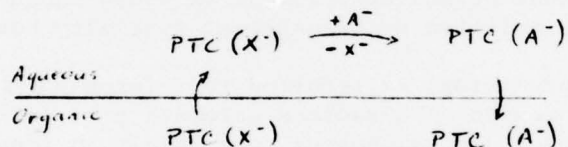
During the past few years, the increasing interest in phase transfer catalysis (sometimes known as ion pair partition) influenced the development of the current investigation by offering means to bypass the shortcomings already noted. References (i) through (q) describe the basic chemistry of phase transfer catalysis. Accordingly, this report describes the utilization of this concept for improvement of corrosion protection characteristics of paints and preservatives, as well as sealant cure, an unexpected application.



## CHEMISTRY OF PHASE TRANSFER CATALYSIS

Phase transfer catalysis is a technique used essentially by organic preparative chemists. In the past few years it has become increasingly popular due largely to the work of Makosza, Brandstrom, Starks and others (references i to g inclusive). Its versatility, simplicity and speed, coupled with the fact that anhydrous solvents are not required, make this synthetic technique especially attractive industrially.

As the name might imply, phase transfer catalysis is carried out in a two phase aqueous-organic solvent system. The two phases are usually water which contains the anion to be transferred and methylene chloride which contains the phase transfer catalyst (PTC). Due to its slight solubility in water, a small amount of PTC diffuses into the **aqueous phase** where it is able to exchange its original anion ( $X^-$ ) for the anion to be transferred ( $A^-$ ). The PTC with its new anion is then able to diffuse back into the organic phase.



The extent to which any one step of this sequence occurs is determined by equilibrium, but because the solubility of PTC in the aqueous phase is small, nearly all of the original PTC may be finally associated with  $A^-$  in the organic phase. This will occur if the presence of  $A^-$  in the organic phase is the preferred state. It is thought that anions of low charge density are preferred - that is, bromide would be preferred over chloride, etc. Such a technique invites the use of PTC to catalyze a substitution reaction carried out in the organic phase, where  $A^-$  substitutes for  $X^-$  in a dissolved organic reactant. The by product  $X^-$  is transferred to the aqueous phase by the PTC where it is exchanged for  $A^-$  and the sequence repeated until total equilibrium is established.

In this work the primary objective is to transfer a chromium VI-containing anion to an organic phase not for subsequent chemical reaction but for availability as a soluble corrosion inhibitor. The actual mechanism of inhibition in an organic coating formulated with soluble inhibitor is not known but probably would involve aqueous leaching of the anion to the substrate interface and subsequent chemisorption of the solubilized inhibitor onto the substrate.

## RESULTS

1. Of the 11 phase transfer catalysts (PTC's) tested, 8 exhibited chromium VI transfer into chlorinated solvents (methylene chloride and chloroform). Only 1 PTC transferred chromium VI into hexane and toluene. Table I lists the PTC's evaluated, and Tables II and III list the results of these experiments.

TABLE I  
Phase Transfer Catalysts

Code	PTC
1	Tetraethylammonium chloride (monohydrate)
2	Tetraethylammonium bromide
3	Methyltributylammonium iodide
4	Tetrabutylammonium chloride
5	Tetrabutylammonium iodide
6	Cetyltrimethylammonium bromide
7	Benzyltrimethylammonium bromide
8	Benzyltriethylammonium chloride
9	Benzyltriethylammonium bromide
10	Benzyltriphenylphosphonium chloride
11*	Methyltrialkyl ( $C_8 - C_{10}$ ) ammonium chloride

\*Code 11 is a product of Ashland Chemical Company, a Division of Ashland Oil, Inc. whose product is designated Adogen<sup>®</sup> 464.

TABLE II  
Chromate Transfer

Aqueous Phase = 43% Sodium Chromate

Organic Phase	Methylene Chloride	Chloroform	Hexane	Toluene
PTC Code				
1	-	-	*	*
2	-	-	*	*
3	-	-	*	*
4	✓	✓	*	*
5	-	-	*	*
6	-	✓	*	*
7	*	-	*	*
8	-	-	*	*
9	-	-	*	*
10	✓	✓	*	*
11	✓	✓	✓	✓

- Indicates no visible transfer of Cr VI

✓ Indicates significant transfer of Cr VI

\* Indicates PTC insoluble in organic phase

TABLE III

## Dichromate Transfer

Aqueous Phase = 67% Sodium Dichromate

Organic Phase	Methylene Chloride	Chloroform	Hexane	Toluene
PTC Code				
1	-	-	*	*
2	-	-	*	*
3	✓	✓	*	*
4	✓	✓	*	*
5	✓	✓	*	*
6	✓	✓	*	*
7	*	-	*	*
8	✓	✓	*	*
9	✓	✓	*	*
10	✓	✓	*	*
11	✓	✓		

- Indicates no visible transfer of Cr VI
- ✓ Indicates significant transfer of Cr VI
- \* Indicates PTC insoluble in organic phase



2. A new class of organic corrosion inhibitor has been prepared at high yield using methltrialkyl ( $C_8 - C_{10}$ ) ammonium chloride. Chromium analysis shows that the new inhibitor contains 11.0 per cent or approximately 1.1 moles Cr per mole phase transfer catalyst.
3. The new inhibitor has been rendered stable at room temperature by evaporation of the carrier solvent, methylene chloride. The resulting product is a clear, brown viscous syrup hereinafter called soluble dichromate or SDC.
4. SDC is soluble in aromatic and chlorinated hydrocarbon, alcohols, ketones, and acetates but insoluble in aliphatic and cycloaliphatic hydrocarbons. All organic solutions gradually discolor or show precipitates; the presence of moisture in the solution has been found to accelerate the degradation.
5. Modification of MIL-C-85054 (Amlguard) corrosion preventive compound with 1 percent by weight of SDC improved the corrosion resistance of the preservative by 200% when applied to 1010 steel coupons and tested in salt spray. Additional salt spray and storage stability tests are underway (Figure 1).
6. The following materials modified with an earlier, less active version of SDC (0.10 per cent Cr VI as opposed to 11.0 percent) exhibit promising improvement in their ability to protect aircraft metals in long term salt spray tests: epoxy/polyamide coatings (Figure 2), MIL-E-5557 alkyd enamels (Figure 3), MIL-E-81309 corrosion preventive compound (Figure 4).
7. When SDC was used as an oxidative accelerator for MIL-S-8802 polysulfide sealant, application time was 4-5 minutes, indicative of rapid curing. However, the cured sealant exhibited considerable softening at elevated temperatures; this phenomenon has been attributed to plasticization by the phase transfer catalyst and may be mitigated by the use of a lower molecular weight catalyst.



FIGURE 1. Soluble Dichromate Modified MIL-C-85054 Preservative (A = 0.11% Cr, B = 0.011% Cr, C = 0%) after 213 Hours Exposure to 5% Salt Spray; Substrate = 1010 Steel.





FIGURE 2. Soluble Dichromate Modified Epoxy/Polyamide Coating (A = 0.06% Cr, B = 0% Cr) after Five Months Exposure to 5% Salt Spray, Substrate = 1010 Steel.

B



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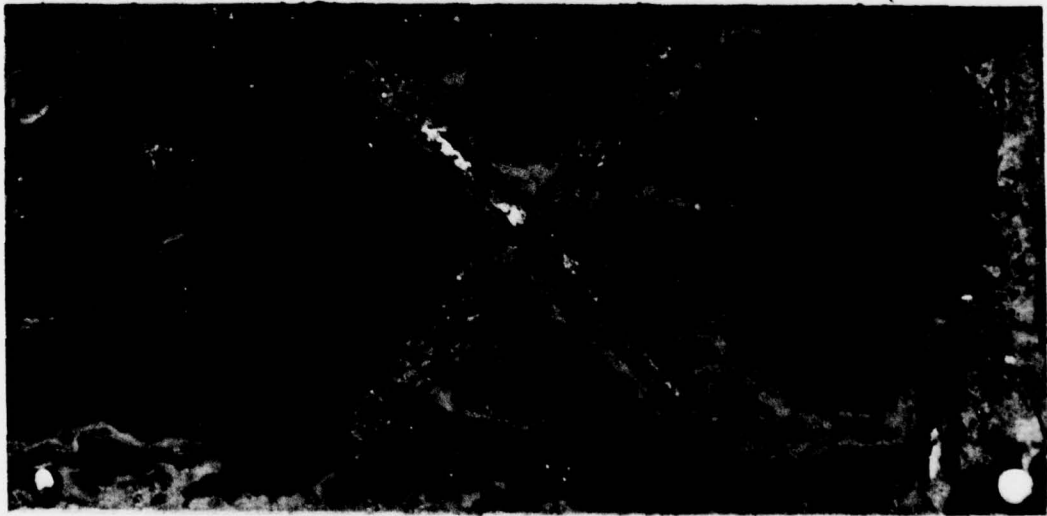


FIGURE 3. Soluble Dichromate Modified MIL-E-5557 Alkyd Enamel (A = 0.06% Cr, B = 0% Cr) after Four Months Exposure to 5% Salt Spray; Substrate = 1010 Steel.



FIGURE 4. Soluble Dichromate Modified MIL-C-81309 Corrosion Preventive Compound (A = 0.02% Cr, B = 0% Cr) after Six Days Exposure to SO<sub>2</sub>/Salt Spray; Substrate = 1010 Steel.

## DISCUSSION OF RESULTS

An early attempt to form a complex containing Cr VI by direct transfer from crystalline potassium dichromate to methylene chloride using Adogen 464 produced a very dilute Cr VI solution, where the molar ratio of Cr to Adogen 464 was about 0.05 (Note 1). In spite of the relatively small Cr content and, therefore, the significant chloride content, this dilute solution was used to modify several organic coatings. Surprisingly, significant differences in salt spray resistance were obtained. This sparked efforts to increase the Cr content and thereby reduce chlorides.

SDC in the form now being evaluated is prepared, as explained above, by transfer of chromium VI from an aqueous phase to an organic phase using the phase transfer catalyst methyltrialkyl ( $C_8 - C_{10}$ ) ammonium chloride known also as Adogen 464. As prepared by this procedure, the final product had a molar ratio of chromium to Adogen 464 of about 1.1, or 22 times the chromium content of the earlier product. When the methylene chloride carrier solvent is evaporated, a stable brown syrup results containing 11.0 per cent chromium by weight.

Ultraviolet spectroscopic data indicate that the anion associated with the phase transfer catalyst is the dichromate anion.

		$\lambda_{\max}$ (m $\mu$ )	$E_{\max}$ (moles/liter-cm)	
Bichromate	$HCrO_4^-$	350	1600	Reference r
Dichromate	$Cr_2O_7^{=}$	373	4130	"
		270	7100	"
Chromate	$CrO_4^{=}$	373	4790	"
		270	3650	"
	Soluble	373	4120	This work
	Chromate	270	7710	"

$HCrO_4^-$  does not exhibit maximum absorption at the proper wavelengths, and  $CrO_4^{=}$  exhibits too small an extinction coefficient at 270 m $\mu$ . Therefore, the complex is postulated to be an ion trio (2).

(Note 1) All calculations requiring the molecular weight of Adogen 464 are performed assuming the phase transfer catalyst to be 100% methyloctylnonyldecylammomium chloride (M.W. = 446)





It is noted, however, that slightly more chromium is present than can be accounted for by this species alone. Undoubtedly a significant amount of (b) also exists.

The stability of SDC in syrup form (that is, exclusive of carrier solvent) has been evaluated by comparing the ultraviolet spectra of two portions of the syrup - one stored at room temperature and one at 50°C (122°F), both for 36 days. After corrections were made for volatile content, the extinction coefficient for the two samples were identical. It was also noted that no color change (indicative of chromium reduction) occurred during a two hour exposure to 105°C (221°F). Previous efforts to produce a Cr VI inhibitor using macrocyclic polyethers were unsuccessful due to oxidation of the polyether by the anion, resulting in the development of a greenish black material.

The oxidizing properties of the SDC were exploited in the cure of a polysulfide sealant base. Roughly, the reaction can be represented as follows:

When the base component of a MIL-S-8802, Class B sealant formulation was cured at 7 parts SDC per 100 parts base, the following data were obtained:

Application time	4-5 minutes
Tack free time	8-10 minutes
Shore A-Z hardness after 2 months	45

However, at 100°C (212°F) the cured sealant could be permanently deformed with light hand pressure. Probably, this is due to plasticization by the phase transfer catalyst. By using a lower molecular weight phase transfer catalyst in the preparation of SDC, higher modulus and less permanent set might be obtained.

Use of SDC in various organic protective coatings has resulted in as much as 200 per cent improvement in salt spray resistance while altering the visual appearance of the film only slightly. To date the most promising application for SDC as an inhibitor is with the preservative MIL-C-85054, a material specifically designed to be colorless and clear. It was during the testing of this preservative that small blisters containing chromates were detected, indicating that chromate will indeed leach from the film modified with SDC. The primary significance of SDC is that transparent protective coatings may now be formulated with the benefit of chromate inhibition.

A word of caution, however, must be given regarding the toxicity of SDC. Adogen 464 is labeled an "irritant" and chromates are well known poisons to living tissue and may also be carcinogenic. The toxicity of the soluble chromate itself has never been evaluated.

#### EXPERIMENTAL

##### Preparation of SDC (Soluble Dichromate)

Two solutions are prepared: 50.0 grams of Adogen 464 is dissolved in 250 milliliters of methylene chloride (organic phase = A); 468 grams of sodium dichromate (dihydrate) is dissolved in 312 milliliters of distilled water (aqueous phase = B). A 250 milliliter portion of B is extracted with A in a separatory funnel and discarded. It will be noted that A has become a deep orange due to the formation of Adogen - dichromate complex. The remaining portion of B is contacted with A, which is then isolated and dried with magnesium sulfate (anhydrous). Methylene chloride is then evaporated from the dichromate-laden A which becomes a clear, brown syrup. Evaporation is continued to 2 mm/37°C. The product contains approximately 11.0% chromium.

##### Salt Spray Evaluations

Test specimens were prepared from 1010 steel panels. Prior to coating application, specimens were cleaned by sequential immersion in the following boiling solvents: (1) TT-T-291, (2) TT-T-291, (3) methanol (95%) and (4) methanol (100%). Specimens were then coated as shown in Table IV.



TABLE IV  
EXPERIMENTAL COATINGS

	%Cr	Application (No. Coats)	Film Thickness (Mils)
MIL-C-85054 (Amlguard)	0.011 and 0.11	DIP (2)	1.0
Epoxy Polyamide	0.06	SPRAY	0.8
MIL-E-5557	0.06	BRUSH	1.0
MIL-C-81309	0.02	DIP	0.5

The epoxy polyamide and MIL-E-5557 specimens were air-dried 7 days before exposure in the ASTM standard test method B117 (5% sodium chloride). MIL-C-85054 and MIL-C-81309 specimens were air-dried 24 hours before exposure using the same test method.

### C O N C L U S I O N S

The original objective - to create an organo-soluble corrosion inhibitor using Cr VI - has been accomplished and has resulted in improved corrosion resistance for each protective coating to which soluble dichromate has been added. Although SDC has been used successfully in pigmented coatings, it can impart corrosion resistance to unpigmented clear coatings without affecting transparency.

SDC has been shown to be an efficient oxidizing agent when used to cure a polysulfide sealant base. Other applications for oxidizers where SDC may be useful include catalysts for drying oils and preparative organic reactions requiring Cr VI for oxidation.

### R E C O M M E N D A T I O N S

Preliminary work shows that chromium VI solubilization can be achieved using several phase transfer catalysts. These additional complexes should be isolated and evaluated for inhibitive characteristics as well as curative properties. A lower molecular weight curing agent should minimize the elevated temperature softening of polysulfide sealant. Methods developed in this investigation should serve as a point of departure for solubilizing other inorganic inhibitors and oxidizers. Because complexation with a phase transfer catalyst usually changes the activity of the inorganic salt, experimental results may not be predictable and may, in fact, lead to interesting innovations in the fields of coating technology and elastomers. Therefore, it is recommended that a developmental study be initiated to capitalize on the findings of this effort.

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A C K N O W L E D G E M E N T

The efforts of Mr. C. Nadler to utilize soluble dichromate as a sealant curing agent are appreciated.